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The use of superionic conductors, in particular $Ag_{13}I_9W_2O_8$, as fast, repetitive, optically triggered opening switches for power conditioning applications in spacecraft has been investigated. It was found, unexpectedly, that serious shelf-life degradation in this material exists, caused by conversion of Ag^+ ions to neutral silver. This degradation can be minimized by storage at 150°C or above, but irreversible conversion from $Ag_{13}I_9W_2O_8$ to $Ag_4I_2WO_4$ and $Ag_5IW_2O_8$ is greatly accelerated by the presence of laser light.

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Annual report: ONR/SDIO contract N00014-86-K-0516 (CU #1534705)

"Superionic Conductors as Fast, Repetitive Opening Switches"

ABSTRACT

The use of superionic conductors, in particular $Ag_{13}I_9W_2O_8$, as fast, repetitive, optically triggered opening switches for power conditioning applications in spacecraft has been investigated. It was found, unexpectedly, that serious shelf-life degradation in this material exists, caused by conversion of Ag^+ ions to neutral silver. This degradation can be minimized by storage at 150^0C or above, but irreversible conversion from $Ag_{13}I_9W_2O_8$ to $Ag_4I_2WO_4$ and $Ag_5IW_2O_8$ is greatly accelerated by the presence of laser light.

Technical report:

In this, the second year of our research on the use of superionic conductors as fast, repetitive opening switches, we have carried out the following steps of our program:

1) We designed, tested and made measurements with two pulsed laser systems: The first is a 7 ns, 2MW pulsed excimer laser used to drive a rhodamine dye laser. With this system we successfully measured the photoconductive response of our superionic conductor $Ag_{13}I_9W_2O_8$ and determined that the response time was faster than 5 ns and that the sign of the photoconductivity was negative; i.e., the material became more insulating when exposed to laser light. This confirmed our basic hypothesis regarding the mechanism of optical response in $Ag_{13}I_9W_2O_8$ as involving photoproduction of electron-hole pairs, with subsequent $e + Ag^+ \rightarrow Ag^0$ neutralization. This showed that the use of $Ag_{13}I_9W_2O_8$ as a fast opening switch was indeed feasible.

2) Unfortunately, we discovered an unexpected and very serious shelf-life degradation in this material. When stored under ambient conditions $Ag_{13}I_9W_2O_8$ decomposes into $Ag_4I_2WO_4$ and $Ag_5IW_2O_8$. The latter two materials are not superionic conductors and have no apparent use as fast, repetitive, optical opening switches. We have found that storage at temperatures above 150^oC prevents this spinodal decomposition. Similar high temperature storage is required for other well-studied Ag-ion conductors, especially the popular $RbAg_4I_5$ electrolyte. A complete phase diagram for the AgI/Ag_2WO_4 system is shown in Fig. 1 on the following page, after Takahashi. Independently and at about the same time as our own work, this shelf-life degradation problem in $Ag_{13}I_9W_2O_8$ (sometimes still labeled $Ag_6I_4WO_4$ after its initial, preliminary phase determination in 1973) was analyzed by Suthanthiraraj at the University of Madras. In his work, which was intended to further the use of this compound as the electrolyte in solid state batteries, he found that the power output was 85% less after 125 days of shelf-storage at ambient temperatures.

3) Optical damage: By storing the specimens at elevated temperatures, we were able to minimize the decomposition described above and prolong the shelf-life. However, as soon as the materials were subjected to repetitive optical illumination from the pulsed lasers to measure the speed and magnitude of their photoconductivity, the laser illumination itself greatly accelerated the spinodal decomposition into non-functional $Ag_4I_2WO_4$ and $Ag_5IW_2O_8$. Our conclusion, therefore, is that this material cannot be made into a functional fast, repetitive opening switch, except by maintaining it in a controlled temperature environment between 150 and 295^{o}C, which we regard as impractical.

4) Conclusions and directions for the final year of the project: We are attempting to grow large single crystals of $Ag_{13}I_9W_2O_8$ under several atmospheres of pure oxygen. It is known that single crystals of order 1 cc can be prepared in this way. We will attempt to see to what degree spinodal decomposition in such single crystals is inhibited. Since funding for the third year of this project has been reduced nearly to zero, a limited number of man-hours will be devoted to wrapping up the project and preparing a final publication summarizing the results (probably for the Journal of Applied Physics).

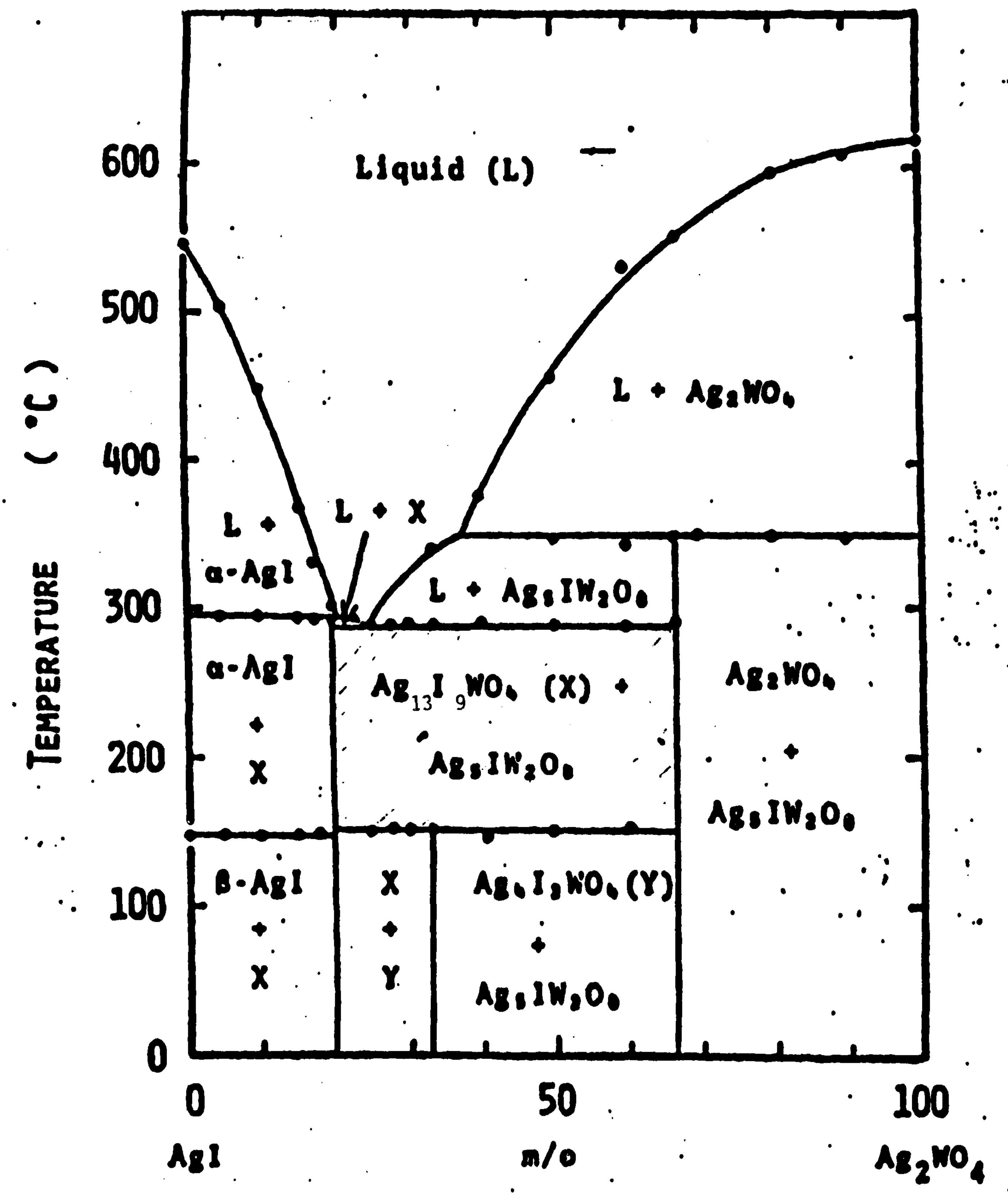

Fig. 1. Phase diagram of the system AgI-Ag_2WO_4

Degrees produced under this contract:

Two students, Mr. David Atkins and Mr. Bradley Melnick, have completed the requirements for the M. S. degree in physics; these masters degrees (without thesis) will both be awarded at the August 1988 graduation. Both Mr. Atkins and Mr. Melnick were supported primarily by this ONR/SDIO grant over the two years of graduate study they have completed at the University of Colorado.

Publications produced under this contract:

"Superionic Conductors as Fast, Repetitive Opening Switches," J. F. Scott and B. M. Melnick, SPIE vol. 871 (Space Structures, Power, and Power Conditioning), pp.153-156 (1988).

(reprint attached)

Superionic conductors as fast, repetitive opening switches*

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ABSTRACT

When subjected to modest levels of illumination (1W/cm^2) of green light, the fast-ion conductor $Ag_{13}I_9W_2O_8$ exhibits an order of magnitude decrease in conductivity. This effect is fast and repetitive, but experiments reveal problems with the material in the form of serious aging (shelf-life) effects that are accelerated in the presence of strong illumination.

1. INTRODUCTION

There is a perceived need for a fast repetitive opening switch for a variety of applications. Many fast closing switches exist, including optical devices driven by laser triggers and photoelectric effects. However, most fast opening switches are essentially fuses and are therefore not repetitive.

In 1978, in this laboratory, an unexpected effect was found[1] in a fast-ion conductor ("superionic" conductor) $Ag_{13}I_9W_2O_8$: The electrical conductivity decreased by approximately an order of magnitude when the material was illuminated with relatively modest power (~1W/cm^2) of green 514.5nm light from an argon ion laser, as shown in fig. 1. In most materials there is either no change in conductivity in the presence of such illumination, or else there is small increase in conductivity due to the photoproduction of electron-hole pairs (the usual photoelectric effect):

$$\hbar\omega_{laser} \rightarrow e^- + h^+ \tag{1}$$

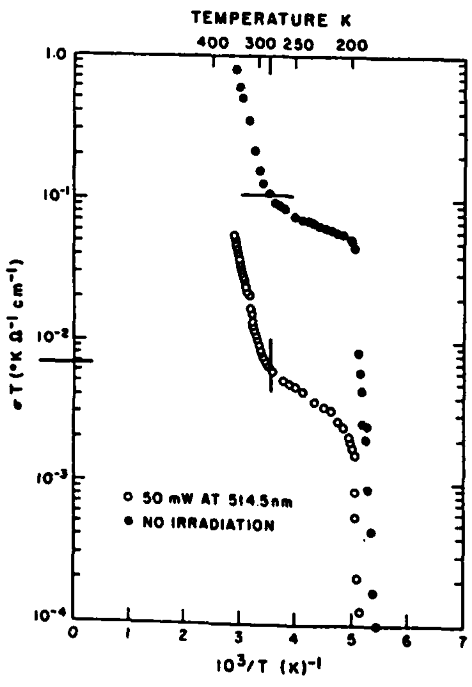

Figure 1. Electrical conductivity σ times temperature T versus $^1/T$ for $Ag_{13}I_9W_2O_8$ with and without ~1W/cm^2 of 514.5nm illumination (Ref. 1).

In $Ag_{13}I_9W_2O_8$ it was hypothesized that the optical effects were more complicated. This material is electonically insulating, but it has a sufficiently large ionic mobility for diffusion of silver ions that its ionic conductivity (~1 ohm^{-1}cm^{-1}) is in the range suitable for use as electrolyte material in solid state batteries.[2] Such Ag/$Ag_{13}I_9W_2O_8$/AgCl cells have use in devices such as pacemakers for implantation in heart-disease patients and in computer timing and memory circuits, where their small size and weight compensates for their greater cost in comparison with other batteries.[3]

The mechanism hypothesized for the observed decrease in conductivity in $Ag_{13}I_9W_2O_8$ under illumination is given as

$$\hbar\omega_L + Ag^+ \rightarrow e^- + h^+ + Ag^+ \tag{2}$$

as in Eq. (1), followed by

$$e^- + h^+ + Ag^+ \rightarrow h^+ + Ag^o, \tag{3}$$

the neutralization of a silver ion by the photoexcited conduction electron. This reaction was initially observed to be fast with respect to times that could be measured with a mechanically chopped laser beam (~1ms), and if Eq. (3) is correct, it should be <1ns, since it is an electronic process, not a thermal one. The process was observed to be highly reversible, though not completely so, since neutral Ag^o was seen to plate out on the surface of the $Ag_{13}I_9W_2O_8$ single crystal used for the measurements.

The kinetics outlined in Eqs. (2,3) could explain qualitatively the observed decrease in conductivity under illumination, since each laser photon removes one

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charge carrier (Ag^+ ion) from the system when it is absorbed, but a quantitative analysis of the data implies that something more complex and interesting must be involved. One watt of green laser light per cm^2 is $\sim10^{17}$ photons/s incident on the crystal. If 50% of them are absorbed, that still results in $Ag^+ \rightarrow Ag^o$ conversion of only $\sim10^{-3}$% of the carriers, too small a fraction to account for the observed percentage decrease in conductivity, assuming that the

$$Ag^o \rightarrow Ag^+ \tag{4}$$

reconversion occurs $\leq$1ms (required as an upper limit from the preliminary chopper measurements). Stated in another way, the process hypothesized in Eq. (1,3) requires an effective quantum efficiency much greater than 100% to account for the experimental data. Is this in some way possible? We show below that there is a plausible reconciliation of this apparent paradox.

2. THE MATERIAL

$Ag_{13}I_9W_2O_9$ was first prepared[4] by Takahashi at Nagoya University. He determined the complete phase diagram for the AgI/Ag_2WO_4 system and found that one particular phase had particularly attractive superionic conductivity and chemical stability. He fabricated solid state batteries with this material as the electrolyte and determined its probable formula to be $Ag_6I_4WO_4$. This material is still often referred to by that formula, but Chan and Geller[5] later showed via careful x-ray crystallography studies that it is $Ag_{13}I_9W_2O_8$. The structure of this compound is shown in fig. 2a and 2b. Notable is the fact that the tungsten ions are octahedrally coordinated $(W_4O_{16})^{-8}$ complexes, rather than the more common $(WO_4)^{-2}$ tetrahedra. Fig. 2 also shows two of the conduction pathways permitted for Ag^+ ions. These pathways are typologically one dimensional ("pretzel-like") although they are geometrically three dimensional with respect to the crystallographic a, b, c lattice directions. That means they are easily jammed up, a point to which we return below.

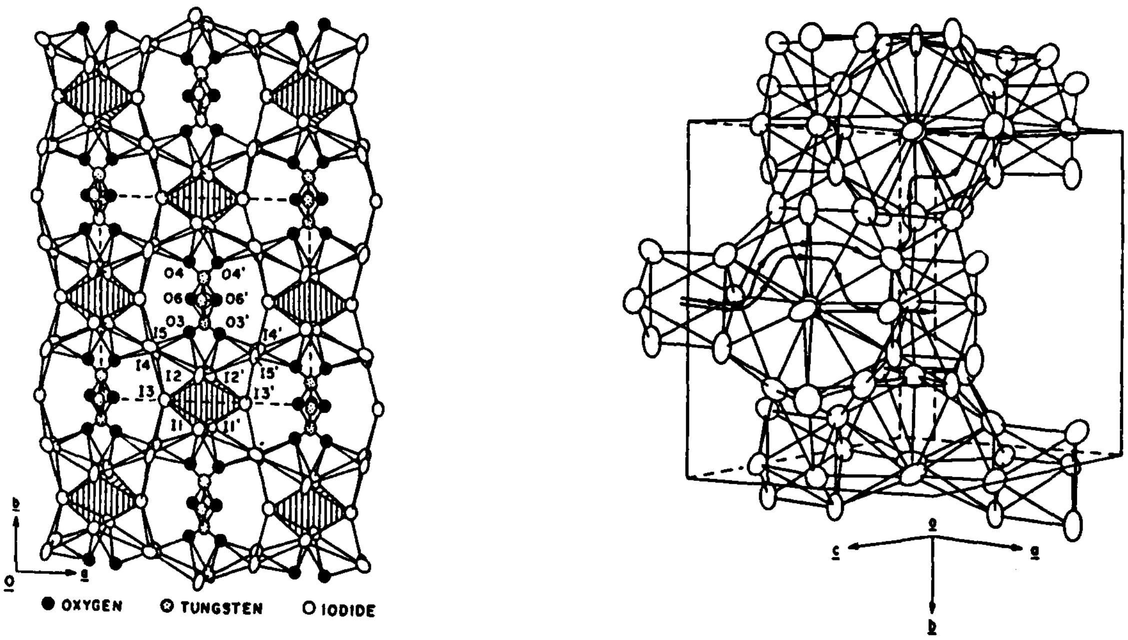

Figure 2. Structure of $Ag_{13}I_9W_2O_8$: a) ab-plane; b) showing Ag^+ ion conduction channels (Ref.5).

Neutral silver Ag^o is 15% larger than Ag^+. Thus, when $Ag^+ \rightarrow Ag^o$ is optically converted, not only is one charge carrying Ag^+ ion removed from the system, but one conduction channel, illustrated in Fig. 2, becomes blocked. This can multiply the effect of each photoexcitation process Eq. (3) by $\sim 10^5$. (Recall that a lcc crystal has $\sim 10^7$ Ag^+ ions in each direction x, y, z.) This channel blocking could account for the surprisingly large decrease in conductivity noted originally.[1]

3. NEW EXPERIMENTS

We have set out to explore the kinetics of this unusual optical system by using pulsed lasers to determine the speed of the device as an opening switch

$$\hbar\omega_L + Ag^+ \rightarrow e^- + h^+ + Ag^+ \rightarrow h^+ + Ag^o \tag{5}$$

(note that the hole mobility is negligible in Eq. (5) so that one carrier is removed per incident photon)

and the speed of the re-ionization

$$Ag^o \rightarrow Ag^+ + e^- \tag{6}$$

We also wish to determine the dependence of reaction rates in Eqs. (5,6) upon laser wavelength, laser power density, and sample temperature.

Unfortunately, in the course of attempting these measurements over the past 18 months, we have discovered something previously unsuspected[4,5] - that $Ag_{13}I_9W_2O_8$ has a poor shelf-life. It degrades by irreversible conversion of Ag^+ ions to Ag^o. We have examined specimens from three sources: Geller at the University of Colorado, Takahashi at Nagoya, and Suthanthiraraj in Madras. In none of these samples were we able to reproduce the original results. Typical photoconductivity data are shown in Fig. 3. A small increase in conductivity is shown for the illuminated specimen, compared with the dark value.

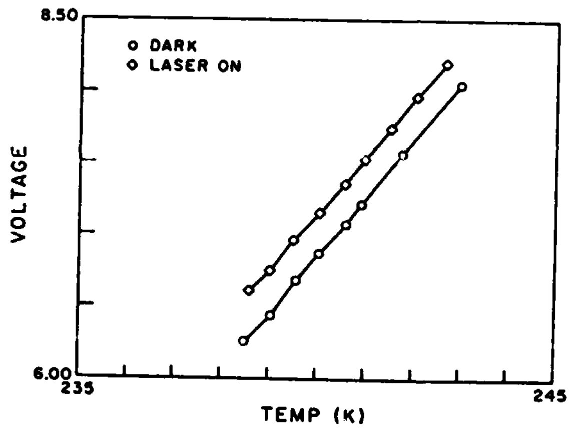

Figure 3. New measurements of electrical conductivity in $Ag_{13}I_9W_2O_8$, with and without illumination, showing conventional photoconductivity effects. (Voltage drop over a load resistor proportional to photoconductivity.)

These results are compatible with the very recent results[6] of Suthanthiraraj, shown in Fig. 4. He finds very rapid shelf-life degradation for $Ag_{13}I_9W_2O_8$ in use as a solid state battery. The internal resistance increased from 0.82 x 106 ohm-cm at 50 days to 4.43 x 106 at 125 days. This increase can be attributed to $Ag^+ \rightarrow Ag^o$ conversion. For studies such as ours this effect is worsened by an accelerated aging phenomenon: The laser light causes preferential plating of neutral silver on the ±c faces of the sample. This is presumably due to photovoltaic effects along the ferroelectric axis. For these reasons our attempts to measure switching time and recovery time have been stalled. We are now attempting to grow our own single crystals (large single crystals can be grown under several atmospheres of oxygen) and to look for similar effects in other silver superionic conductors, such as $RbAg_4I_5$.

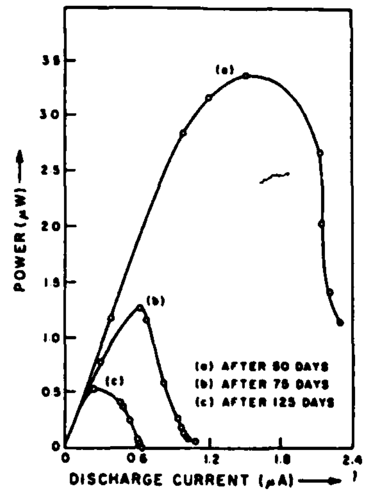

Figure 4. Shelf-life degradation of $Ag_{13}I_9W_2O_8$ in solid state batteries (Ref. 6).

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